Supporting Information

Design of an Active and Durable Catalyst for Oxygen Reduction Reactions Using Encapsulated Cu with N-Doped Carbon Shells (Cu@N-C) Activated by CO₂ Treatment

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Experimental section

Catalyst synthesis

Synthesis of Cu@N-C(hydro). Sucrose ($C_{12}H_{22}O_{11}$, 2.7 g), copper(II) nitrate trihydrate ($(Cu(NO_3)_2 \cdot 3H_2O, 1.5 g)$ and ammonium sulfate ($(NH_4)_2SO_4$, 2.1 g) were used as the precursors of carbon, copper and nitrogen species, respectively. As the process of hydrothermal synthesis, these precursors were added into 45 ml Teflon vessel with 30 ml mili-Q water and stirred by magnetic bar for longer than 3 h. Subsequently, the Teflon vessel was transferred into an autoclave, and then heated at 180 °C for 8 h. After cooling down the autoclave, the synthesized material was filtered by a Milli-Q water. The powder was sufficiently dried in a dry-oven at 80 °C for 5 h, and then ground for the synthesis of the next

step. **Synthesis of Cu@N-C(heat).** To graphitize the carbon materials, Cu@N-C(hydro) power on alumina boat was kept at 1000 $^{\circ}$ C and 2 h under Ar atmosphere and then cooled down. **Synthesis of Cu@N-C(CO₂).** As-synthesized Cu@N-C(heat) material was again kept at 1000 $^{\circ}$ C for 15 min, and CO₂ gas of 1 bar was filled in the quartz tube to oxidize the carbon species. Cu@N-C power was cooled down under Ar atmosphere. The catalysts were consecutively synthesized from Cu@N-C(hydro) to Cu@N-C(CO₂), and a series of the preparation was illustrated in Fig. S1 (Supporting Information). **Synthesis of N-C(CO₂).** The synthesis processes of N-C(CO₂) were identical to that of Cu@N-C(CO₂) except for the absence of Cu precursor.

Preparation of catalyst ink

Cu@N-C catalysts (0.6 mg/cm²): Each 10 mg of as-synthesized Cu@N-C catalysts was mixed with 150 µL Milli-Q water, 150 µL ethanol, and 50 µL of 5 wt.% Nafion[®]. After sonication for 2 h, the suspension ink solution of 5.9 µL was loaded on glassy carbon electrode ($\phi = 6$ mm) using a pipette to acquire the loading amount of 0.6 mg/cm².

Pt/C (20 μ g_{Pt}/*cm*²): 8.8 mg of 46 wt.% Pt/C catalyst (commercially available Pt TEC10E50E, purchased from Tanaka Kikinzoku Kogyo (TKK) Corp., Japan) was mixed with 1130 μ L Milli-Q water, 257 μ L isopropanol and 92 μ L of 5 wt.% Nafion[®]. After sonication for 2 h, the suspension solution of 2.1 μ L was loaded on glassy carbon electrode (ϕ =6 mm) using a pipette to acquire the amount of 20 μ g_{Pt}/cm².

Electrochemical analysis

Electrochemical measurements were performed in three-electrode electrochemical cell with ALS/Chi 760Ds electrochemical analyzer. Rotating ring disk electrode voltammetric

measurements were carried out at a scan rate of 5 mV/s with varying rotating speeds from 400 to 2500 rpm at N₂ or O₂-saturated 0.1M KOH. Reference and counter electrode were Ag | AgCl | KCl_(sat.) electrode and graphite plate, respectively. For the working electrode, we modified glassy carbon electrode by loading various catalysts such as Cu@N-C(hydro), Cu@N-C(heat), Cu@N-C(CO₂), N-C(CO₂), and Pt/C. The number of electrons (*n*) involved with ORR and H₂O₂ production percentage (%) were defined as the following equations, respectively:

$$n = \frac{4I_{\rm D}}{I_{\rm D} + (I_{\rm R} / N)}$$
(S1)

$$H_2O_2(\%) = 100x \frac{2I_R / N}{I_D + (I_R / N)}$$
 (S2)

where, $I_{\rm R}$ and $I_{\rm D}$ are, respectively, ring and disk currents, respectively. The collection efficiency (*N*) was 0.37 in this study.

The kinetic current (J_k) and *n* could be derived from Koutecky-Levich plot (K-L plot).

$$\frac{1}{J} = \frac{1}{J_{\rm L}} + \frac{1}{J_{\rm K}} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_{\rm K}}$$
(S3)

$$B = 0.62 n F C_0 D_0^{2/3} v^{-1/6}$$
 (S4)

where *J* is the measured current density, and *B* is Levich slope. $J_{\rm K}$ and $J_{\rm L}$ are, respectively, the kinetic current density and the diffusion limited current density. *F* is the Faraday's constant (96485 C · mol⁻¹), C_0 is the bulk concentration of dissolved oxygen in the electrolyte (1.2x10⁻⁶ mol · cm⁻³) in 0.1 M KOH solution, D_0 is the diffusion coefficient of oxygen (1.9x10⁻⁵ cm²s⁻¹), *v* is the kinetic viscosity of the electrolyte (1.13x10⁻² cm²s⁻¹).¹

Characterization

The structural properties of Cu@N-C catalyst were characterized using a field-emission scanning electron microscope (FE-SEM, Hitachi S-5500) at 5 kV, a transmission electron microscope (TEM, HITACHI H-8100) at 200 kV. The measurements of a high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM, JEOL JEM-2100 LaB₆) at 200 kV and an energy-dispersive X-ray spectroscopy (EDS, JEOL JED-2300) were carried out. X-ray diffraction (XRD) was performed on a Rigaku RINT-2100 diffractometer using Cu K α radiation (λ =1.5418 Å) at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCA-3400 Mg K α (1253.6 eV) source. Acceleration voltage and emission current of XPS are 10 kV and 20 mA, respectively. The Brunauer-Emmett-Teller (BET) specific surface areas of catalysts were measured by N₂ adsorption using a volumetric adsorption measurement instrument (Bel Japan, Belsorp-mini II). BET surface areas of Cu@N-C(heat), Cu@N-C(hydro) and Cu@N-C(CO₂) are 1, 526 and 542 m²/g, respectively.

Computational details

Vienna Ab-initio Simulation Package (VASP) was utilized to calculate the total ground state energies, and optimize the structures of the catalysts.² The projector augmented wave (PAW) pseudo-potential³ was employed to replace the interactions among core electrons,⁴ and the spin-polarized generalized gradient approximation (GGA)⁵ was applied to describe the exchange-correlation energy of electrons as implemented in VASP.⁶ The effect of van der Waals (vdW) energies was considered. Kohn-Sham plane waves were expanded with a cut-off energy of 520 eV in all the calculations. The model for a Cu@N-C nanoparticle was setup by cluster model system with vacuum thickness in unit cell (with approximately 10 Å in threedimensional space). The gamma point mesh of 1 x 1 x 1 k-point was applied to integrate Brillouin zone. The numbers of grid-points for fast Fourier transform (FFT) were 1024 x 1024 x 1024 in x, y, z direction. Bader charge analysis was used to calculate the number of valence electrons for each atom in the Cu@N-C catalysts.

Oxygen binding energy and nitrogen doping energy were defined in Equations (S5) and (S6).

$$E_b = -(E_{catalyst-O} - E_{catalyst} - E_O)$$
(S5)

where, E_b is oxygen binding energy. $E_{catalyst-O}$, $E_{catalyst}$ and E_O are the energies of oxygen adsorbed catalyst, pure catalyst and oxygen atom, respectively.

$$E_{dop}^{n} = E_{Cu@N_{n}C} - E_{Cu@N_{n-1}C} - E_{C} - E_{N}$$
(S6)

where, E_{dop}^n is the doping energy including the number of nitrogen, *n*. $E_{Cu@N_n-C}$ and $E_{Cu@N_{n-1}-C}$ are the ground state energies of Cu@N-C consisting of *n* and *n*-1, respectively. E_C and E_N are the calculated energies of graphitic carbon and nitrogen (1/2 N₂), respectively. In Fig. S10 and Table S2, both the first and the second N doping sites were identified in the pentagonal ring of carbon shell such as N₁, N_{N8}, and N_{N10}. Hence, we allocated N atoms in those locations with doping level of 2.1 at%, considering experimental N-doping level 1.8%. Our DFT model system is composed of total 295 atoms (55 Cu, 236 C and 4 N atoms) and the size is about 1.5 nm.



Fig. S1 Schematic diagram for the process designing Cu@N-C catalysts.



Fig. S2 Pictures of prepared Cu@N-C catalysts; (a) Cu@N-C(hydro), (b) Cu@N-C(heat) and (c) Cu@N-C(CO₂). Cu@N-C(heat) and Cu@N-C(CO₂) powders in alumina boat were shown in (d) and (e), respectively.



Fig. S3 (a) STEM and (b) HAADF-STEM images of Cu@N-C(CO₂). TEM images of Cu@N-C(CO₂) from (c) to (f). TEM images of (g) Cu@N-C(heat) and (h) Cu@N-C(CO₂). HR-TEM images of (i, j) Cu@N-C(CO₂).



Fig. S4 XPS analysis of overall survey spectra. The following materials were measured in the range of 0 to 1000 eV: (a) Cu@N-C(hydro), (b) Cu@N-C(heat), (c) Cu@N-C(CO₂) and (d) N-C(CO₂).



Fig. S5 XPS analysis of copper 2p peaks. The following materials were measured in the range of 924.84 to 975.05 eV: (a) Cu@N-C(hydro), (b) Cu@N-C(heat) and (c) Cu@N-C(CO₂) and (d) N-C(CO₂).



Fig. S6 XPS analysis of nitrogen 1s peaks. The following materials were measured in the range of 389.85 to 410.05 eV: (a) Cu@N-C(hydro), (b) Cu@N-C(heat), (c) Cu@N-C(CO₂) and (d) N-C(CO₂).



Fig. S7 X-ray diffraction (XRD) patterns of Cu@N-C materials; (a) Cu@N-C(hydro), (b) Cu@N-C(heat), (c) Cu@N-C(CO₂) and (d) N-C(CO₂).



Fig. S8 Koutechy-Levich plots on Cu@N-C(CO₂) catalyst. The various potentials from 0.5 to 0.7 V with 0.05 V interval were colored to magenta, green, blue, red and black, respectively.

	Onset potential ^{a)} vs. RHE (<i>E</i> _{onset})	Half-wave potential vs. RHE (<i>E</i> _{1/2})	n at 0.6 V vs. RHE	H ₂ O ₂ (%) at 0.6 V vs. RHE
Cu@N-C(CO ₂)	0.94 (-) ^{b)}	0.83 (-)	3.95 (-)	2.53 (-)
Cu@N-C(Heat)	0.88 (-0.06)	0.72 (-0.11)	3.70 (-0.25)	14.76 (12.23)
Cu@N-C(hydro)	0.77 (-0.17)	0.60 (-0.23)	3.15 (-0.80)	42.75 (40.22)
N-C(CO ₂)	0.87 (-0.07)	0.71 (-0.12)	3.30 (-0.65)	34.15 (31.62)
Pt/C	1.05 (0.11)	0.85 (0.02)	3.92 (-0.03)	3.99 (1.46)

Table S1. ORR activity of Cu@N-C catalysts designed with different processes.

a) Estimated as a potential at which the disk current reaches $10 \,\mu A cm^{-2}$.

b) Deviation from Cu@N-C(CO₂) catalyst.



Fig. S9 Chronoamperometric current-time (i-t) responses obtained at 0.7 V vs. RHE and 1600 rpm for both $Cu@N-C(CO_2)$ and Pt/C catalysts in O_2 saturated aqueous solution of 0.1 M KOH.



Fig. S10 N-doping sites for (a) the first doping sites and (b) second doping sites on Cu@C surface. (c) Oxygen adsorption sites on Cu@N-C catalysts at 2.1 at%.

Table S2. N-doping and O-adsorption energies calculated by DFT method for the atomic sites

 depiected in Fig. S10.

(a) First doping site	Doping energy (meV)	(b) Second doping site	Doping energy (meV)	(c) Oxygen binding site	Oxygen binding energy (meV)
N_1	0.073	N _{N1}	0.496	T _{C1}	3.820
N_2	1.621	N _{N2}	1.274	T _{C2}	3.111
N_3	1.788	N _{N3}	1.552	T _{C3}	3.060
		N _{N4}	0.970	T _{C4}	2.744
		N _{N5}	0.811	T _{C5}	3.132
		N _{N6}	0.778	T _{C6}	3.403
		N _{N7}	0.751	T _N	1.871
		N _{N8}	-0.032	H ₁	3.750
		N _{N9}	0.681	H ₂ ^{a)}	3.820
		N _{N10}	0.027		

^{a)} Oxygen on H_2 site is moved to T_{C1} site after fully relaxed.



Fig. S11 Charge density plots of (a) Empty@N-C and (b) Cu@N-C. Front, side and top views were provided.

Charge density of Cu@N-C





References

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